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LEAD ISOTOPE ANALYSES ON SELECTED CANADIAN MINERAL DEPOSITS

BY

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled LEAD ISOTOPE ANALYSES ON SELECTED CANADIAN MINERAL DEPOSITS, submitted by Paul Joseph Gudjurgis, in partial fulfilment of the requirements for the degree of Master of Science.

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ABSTRACT

A lead isotope study was conducted on several Canadian mineral deposits. New lead isotope data were obtained for the Big Ledge deposit, British Columbia, the Quemont mine, Quebec and the George Lake deposit, Saskatchewan. Some lead models have been proposed to account for the respective lead isotope abundances.

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INTRODUCTION

Systematic variations in lead isotope abundances have proved to be a most useful phenomenon in elucidating the histories of different geological systems. These systematic variations have been applied in lead model studies to obtain quantitative estimates for the age of the earth and its crustal rocks, dates of mineralization of ore deposits and times of orogenies (or regional metamorphisms). Furthermore, lead isotope studies have provided an insight into some of the physical and geochemical properties of these geological systems, be they individual minerals, ore deposits, whole rocks or on a larger scale, the crust itself.

This thesis presents a report on some new lead isotope data obtained by the writer at the University of Alberta from three widely separated areas in Canada - British Columbia, Saskatchewan and Quebec - and embodies interpretations, within the framework of model lead theory, of this data and discussions of some of the geological implications. In addition, a review of some novel observations as reported by Cumming et al (1970) regarding the fractional removal of lead from whole rocks is given.

Lead Isotope Measurements

The Mass Spectrometer

A solid source, single focussing mass spectrometer, (described by Cumming et al (1971)) having a 12" radius of curvature and 90^{o} sector was used in this study. A lead sample was loaded on single tantalum filament and ionized by distillation from the filament when heated. Digital techniques are used to control the magnetic current supply and to read the signal from the mass spectrometer. The mass spectrum is scanned by incremental magnetic field sweeping, this scanning being synchronized with the data reading of the signal which is recorded in digital form on magnetic tape.

Data Analysis

The data reduction techniques have been reported by Cumming et al (1971). The lead isotope data which are recorded on magnetic tape are processed in the following series of operations: The data are filtered; peaks are located; peak heights (adjusted for baseline) are determined along with the respective times; ratios of peak heights are determined by a polynomial fit. The data are processed using an IBM 360 computer.

Considerable attention has been recently focussed by researchers such as Compston and Oversby (1969), Cooper et al (1969) and Ozard and Russell (1970) on the nature and magnitude of fractionation (variable mass

discrimination) and the application of double spiking (isotope dilution) techniques to correct for this phenomenon. Double spiking techniques were not applied by the writer in this study to correct for fractionation effects. However, reruns were made of many individual samples to check the magnitude of fractionation if the absolute values of any isotope ratios were in question.

The content of this thesis is submitted in the following manner: Chapter I deals with lead model theory. Chapters II, III and IV deal with the Wollaston Lake fold-belt, Quemont mine and Big Ledge studies respectively. The summary and conclusions are presented in Chapter V. A description of the procedures employed in extracting and purifying lead is given in the Appendix.

CHAPTER I

LEAD MODEL THEORY

Lead has four stable isotopes, possessing atomic masses of 204, 206, 207 and 208. The lead in the earth is composed of lead which was originally present when the earth was formed (primordial lead) and lead generated by the radioactive decay over geologic time of U^{238}, U^{235} and Th^{232} (radiogenic lead). The isotopes Pb^{206}, Pb^{207} and Pb^{208} are end products of radioactive decay of U^{238}, U^{235} and Th^{232} respectively, while Pb^{204} has no radioactive parent. Thus through radioactive decay the abundance of Pb^{206}, Pb^{207} and Pb^{208} relative to Pb^{204} increases with time.

Parent	Daughter	Decay Constant	Half Life
U^{238}	Pb^{206}	$\lambda = 0.1537\times10^{-9}/yr$	4.49×10^{9} yr
U^{235}	Pb^{207}	$\lambda' = 0.9722\times10^{-9}/yr$	0.713×10^{9} yr
Th^{232}	Pb^{208}	$\lambda'' = 0.0499\times10^{-9}/yr$	13.9×10^{9} yr

The mixture of radiogenic lead and primeval (primordial) lead constitutes common lead and it has, by definition, only a negligible amount of uranium and thorium associated with it. It has been mineralized at some time in the past and the isotopic ratios have not changed since that time.

Multi-Stage Models

Multi-stage lead model theory has been summarized by Kanasewich (1968) and will be reviewed here. The law of radioactive decay is

$$dN = -\lambda N dt \tag{1}$$

where

λ is the decay constant for a particular nucleus;

dN is the number of nuclei out of a total N which decay in a short time dt;

N is the number of atoms at time t.

By convention, the present time is defined as $t = 0$ and time is assigned a positive value in the past. Letting N_o be the number of radioactive atoms at the present time, the solution to (1) is

$$N = N_o\, e^{\lambda t} \quad . \tag{2}$$

The rate of production of Pb^{206} atoms at any time is proportional to the number, $N(U^{238})$, of U^{238} atoms present.

$$\frac{dN\ (Pb^{206})}{dt} = -\ \lambda N(U^{238}) \quad . \tag{3}$$

Dividing both sides of equation (3) by the number of Pb^{204} atoms present and using equation (2),

$$-\ d\ \frac{N(Pb^{206})}{N(Pb^{204})} = \lambda\, [\frac{N_o(U^{238})}{N(Pb^{204})}\, e^{\lambda t}]\ dt \quad . \tag{4}$$

TABLE (1)

SYMBOLS AND CONSTANTS EMPLOYED

Isotope ratio	Present value (t = 0)	Primordial value ($t = t_o$)
Pb^{206}/Pb^{204}	x	$a_o = 9.346$ *
Pb^{207}/Pb^{204}	y	$b_o = 10.218$ *
Pb^{208}/Pb^{204}	z	$c_o = 28.96$ *
U^{238}/Pb^{204}	$\mu = 8.79$ **	$8.79\ e^{\lambda t_o}$
U^{238}/U^{235}	137.8	3.33
Th^{232}/Pb^{204}	$W = 33.7$ ***	$29.7\ e^{\lambda'' t_o}$
	$t_o = 4.578$ **	

* Oversby (1969)

** Cooper et al (1969)

*** Russell (written communication)

Using the symbols defined in Table (1) and integrating equation (4), the total amount of Pb^{206}/Pb^{204} at any time t is given by

$$-\int_{x}^{a_o} dx = \int_{t}^{t_o} \lambda[\mu(t)e^{\lambda t}]dt \; . \tag{5}$$

Solving for x ,

$$x = a_o + \int_{t}^{t_o} \lambda[\mu(t)e^{\lambda t}]dt \; . \tag{6}$$

Similar equations may be obtained for the Pb^{207}/Pb^{204} and Pb^{208}/Pb^{204} ratios

$$y = b_o + \frac{1}{137.8}\int_{t}^{t_o} \lambda'[\mu(t)e^{\lambda' t}]dt \tag{7}$$

$$z = c_o + \int_{t}^{t_o} \lambda''[W(t)e^{\lambda'' t}]dt \; . \tag{8}$$

Kanasewich (1962a) suggested that a quantitative evaluation of the integral equations (6), (7) and (8) may be obtained by treating μ and W to be constants for discrete intervals of time. Since metamorphic or orogenic events are of short duration relative to the half-lives of uranium and thorium, this was thought to be a reasonable assumption. Equations (6), (7) and (8) may then be written in the form

$$x_m = a_o + \sum_{i=1}^{m} \mu_i (e^{\lambda t_{i-1}} - e^{\lambda t_i}) \tag{9}$$

$$y_m = b_o + \frac{1}{137.8} \sum_{i=1}^{m} \mu_i (e^{\lambda' t_{i-1}} - e^{\lambda' t_i}) \tag{10}$$

$$z_m = c_o + \sum_{i=1}^{m} W_i (e^{\lambda'' t_{i-1}} - e^{\lambda'' t_i}) \quad . \tag{11}$$

The most simple form of these equations occurs when only one term appears in the sum of equations (9)-(11).

Single-stage (ordinary leads)

Leads which have evolved in a single closed lead-uranium-thorium system only since the formation of the earth are termed single-stage or ordinary leads. Holmes (1946) and Houtermans (1946) attempted to explain all variations of lead isotope abundances in terms of this restrictive model. They assumed that small regional goechemical heterogeneities developed early in the formation of the earth, but since t_o,lead ratios in a geological system have changed only by addition of radiogenic lead. That is, a particular lead-uranium-thorium system has remained closed to addition or subtraction of lead, uranium and thorium since t_o.

The equations for the measured Pb^{206}/Pb^{204}, Pb^{207}/Pb^{204} and Pb^{208}/Pb^{204} abundances are given by

$$x_1 = a_o + \mu_1 (e^{\lambda t_o} - e^{\lambda t_1}) \tag{12}$$

$$y_1 = b_o + \frac{\mu_1}{137.8} (e^{\lambda' t_o} - e^{\lambda' t_1}) \tag{13}$$

$$z_1 = c_o + W_1(e^{\lambda'' t_o} - e^{\lambda'' t_1}) , \tag{14}$$

where, as indicated in table (1), t_o is the age of the earth; t_1 is the time that lead was mineralized (free of uranium and thorium). Equations (12) and (13) can be combined to give the famous Houtermans isochron equation

$$\frac{y_1 - b_o}{x_1 - a_o} \equiv \phi = \frac{(e^{\lambda' t_o} - e^{\lambda' t_1})}{137.8(e^{\lambda t_o} - e^{\lambda t_1})} \quad . \tag{15}$$

Equation (15) shows that single-stage leads of a common age will be along a straight line in a Pb^{206}/Pb^{204} vs. Pb^{207}/Pb^{204} (x_1 vs. y_1) plot. It is also observed from equations (12), (13) and (14) that single-stage leads of different age will, when plotted as x_1 vs. y_1 or x_1 vs. z_1, define a series of curves (that are functions of time) corresponding to different μ_1 and W_1 values. These curves are called growth curves.

Noting that single-stage leads were closely distributed about a single growth curve, Collins, Russell and Farquhar (1953) postulated that there is a single growth curve to which all single-stage leads fit within a few percent. The assumption was that the μ and W values for the source of these leads were uniform throughout.

Russell (1956) suggested that the mantle was the source of these leads and that the first stage of all

lead development occurred there. Subsequent research has shown that so called "conformable" or "stratiform" deposits represent the closest approximation to single-stage leads. In particular, Stanton and Russell(1959), Russell and Farquhar (1960) and Ostic et al (1967) have discussed the correlation between single stage leads and comformable deposits. Using isotope analyses from known single-stage leads, Ostic et al (1963), Russell and Reynolds (1965) and Cooper et al (1969) have mathematically defined so called primary lead growth curves. The primary growth curve recently calculated by Cooper et al (1969) is currently accepted to be the most precise. When lead isotope data in general are discussed the primary growth curve is often used as a frame of reference.

Most leads in nature have had a more complex history than can be explained by a single-stage model. More elaborate models are required to describe them.

Anomalous leads

Anomalous leads are defined as those leads whose isotopic ratios were produced in two or more distinct lead-uranium-thorium systems. Anomalous leads often plot on a straight line in a Pb^{206}/Pb^{204} vs. Pb^{207}/Pb^{204} graph.

Anomalous leads may be classified into the following types (Kansewich and Farquhar, 1965)

1. Mixtures of two ordinary leads
2. Two stage anomalous lead
3. Short period anomalous lead
4. Simple three stage anomalous lead
5. Higher order multi-stage lead

The general equations for multi-stage leads were given by equations (9), (10) and (11) and are applicable to anomalous lead two-stage models.

For a two-stage model the equations (9), (10) and (11) reduce to

$$x_2 = x_1 + \mu_2 \, (e^{\lambda t_1} - e^{\lambda t_2}) \tag{16}$$

$$y_2 = y_1 + \frac{\mu_2}{137.8} \, (e^{\lambda' t_1} - e^{\lambda' t_2}) \tag{17}$$

$$z_2 = z_1 + W_2 \, (e^{\lambda'' t_1} - e^{\lambda'' t_2}) \quad . \tag{18}$$

The development of a two-stage lead may be visualized to occur in the following manner (Kanasewich, 1962b).

Ordinary lead (single-stage) was differentiated from its source at time t_1 and either formed a lead deposit or was disseminated in the host rock in the crust. At this time the isotopic ratios of the lead were given by x_1, y_1 and z_1 (from the single stage model). Contemporaneously, uranium and thorium entered the same environment. Radiogenic lead developed through the decay of

uranium and thorium. At some later time t_2 remobilization of the lead occurred, mixing the single-stage lead with the radiogenic lead. The isotopic ratios were then "frozen" to the present day. The values x_2, y_2 and z_2 are measured on the mass spectrometer. In general, μ_2 and W_2 will vary for each sample.

One special case of this model occurs for a mixture of two ordinary leads. In this case $\mu_1 = \mu_2$ and $W_1 = W_2$.

Another special case of the two-stage model occurs when the duration of the second stage of lead development is short in comparison to the duration of the first stage. Here the lead isotope ratios will plot on a line nearly tangent to the growth curve (see equation 19).

It may be noted that equations (16) and (17) can be combined to give

$$\frac{y_2 - y_1}{x_2 - x_1} \equiv R = \frac{(e^{\lambda' t_1} - e^{\lambda' t_2})}{137.8\ (e^{\lambda t_1} - e^{\lambda t_2})} \quad . \qquad (19)$$

This equation is mathematically similar to the Houtermans isochron equation. Equation (19) shows that two-stage leads which have the same age but which may have developed in different uranium-thorium environments will be on a straight line in a Pb^{206}/Pb^{204} vs. Pb^{207}/Pb^{204} plot. This line is called an anomalous lead line. The slope R defines the Pb^{207}/Pb^{206} ratio of the radiogenic component.

Three-stage model

The complete equations for a three-stage model have the form

$$x_3 = a_o + \mu_1 (e^{\lambda t_o} - e^{\lambda t_1}) + \mu_2 (e^{\lambda t_1} - e^{\lambda t_2})$$

$$+ \mu_3 (e^{\lambda t_2} - e^{\lambda t_3}) \qquad (20)$$

with similar equations for y_3 and z_3. One particular form of the three-stage model has been adopted to explain the lead isotope abundances of several sulphide deposits. This particular case occurs for $\mu_2 = 0$. Lead development in this case may be imagined to occur in the following manner:

Lead was mineralized at time t_1 as an ordinary lead. At time t_2 uranium and thorium were introduced into the system. Radiogenic lead developed from time t_2 to time t_3. At time t_3 lead was remobilized and the ordinary lead was mixed with the radiogenic lead. The slope of the anomalous lead line becomes

$$\frac{y_3 - y_1}{x_3 - x_1} \equiv R = \frac{[e^{\lambda' t_2} - e^{\lambda' t_3}]}{137.8\ [e^{\lambda t_2} - e^{\lambda t_3}]} \ . \qquad (21)$$

For a complete three-stage model where the uranium concentrations μ_2 and μ_3 vary, the isotopic ratios will scatter about an anomalous lead line (Russell et al, 1966). However for the modified three-stage model just described

where, between times t_1 and t_2 the system is practically free of uranium, the ratios x_3 and y_3 are linearly related. Although upper and lower limits for t_2 or t_3 are readily obtained (Russell and Farquhar, 1960) it is apparent that lead isotope data alone will not provide a unique solution to equation (21) as neither t_2 or t_3 are known. However, given an independent estimate for either t_2 or t_3, equation (21) can be solved. Frequently K-Ar or Rb-Sr radiometric ages are of help in this regard.

Frequently mixed model

As a mathematical exercise, Russell et al (1966) calculated the isotopic compositions for some hypothetical leads as they would have developed in a number of closed uranium-thorium-lead systems. The pertinent expressions for an n-stage model were used. They assumed a binomial distribution for the μ_i (U^{238}/Pb^{204}) values and the μ_i were chosen independently at random from this distribution. The results showed that the frequently-mixed model for lead isotope abundances approximates very closely to a two-stage model.

It should be noted that models with more than a three-stage development have not been successfully applied in case histories to date. The precision of the isotope data is the limiting factor.

A lead model is just a hypothetical history of lead isotope development. The fact that much of the lead isotope data fits patterns predicted by lead model theory provides evidence for its applicability to real geological systems.

CHAPTER II

SOME LEAD ISOTOPE RESULTS FROM THE WOLLASTON LAKE FOLD-BELT, SASKATCHEWAN

Introduction

Cumming et al (1970) have discussed some experimental observations resulting from a heating experiment conducted on a whole rock specimen from the Janice Lake area in the Wollaston Lake fold-belt and have discussed lead isotope data obtained for a suite of galena samples found in the belt. This chapter will review some of the results and present additional data obtained by the writer for sulphide mineralization occurring in the general area. New isotope data will be given for galena in 10 split-core samples from the George Lake zinc deposit located just south of Wollaston Lake and for 3 sulphide samples which appear to be genetically related to the galenas discussed by Cumming et al.

Regional Geology

The general geology of the Wollaston Lake fold-belt system has been described by Money (1968). A detailed summary of the geology is beyond the scope of this thesis. Only a brief outline will be given here.

The Wollaston Lake trend is a major structural and lithological feature in the Churchill geological province extending northeast from the edge of the Canadian Shield through Wollaston Lake and into Manitoba, a distance of some 400 miles (Figure 1). The fold-belt consists of a series of coalescing, isoclinally folded belts. It is bounded on the west and east by granodiorites and granites. Radiometric data indicates that the belt was involved in the Hudsonian Orogeny about 1700-1800 m.y. ago.

Recent discoveries of base metal and uranium mineralization in the area have attracted attention to the economic aspects of the belt.

Local Geology, Janice Lake Vicinity

The geology of the Janice Lake area has been described by Rath (1969) and Rath and Morton (1970). The sequence of metamorphic rocks found in the vicinity of Janice Lake can be subdivided into two major lithologic units which underly more than 90 per cent of the area. The two units consist of associations of variable hornblende-biotite gneisses and biotite gneisses. Mineralization consists of native copper and various copper sulphides and is confined principally to the metaconglomerate horizons associated with the hornblende gneiss unit. The mineralization appears to be of syngenetic sedimentary origin. The particular rock sample of Cumming et al was a hornblende gneiss.

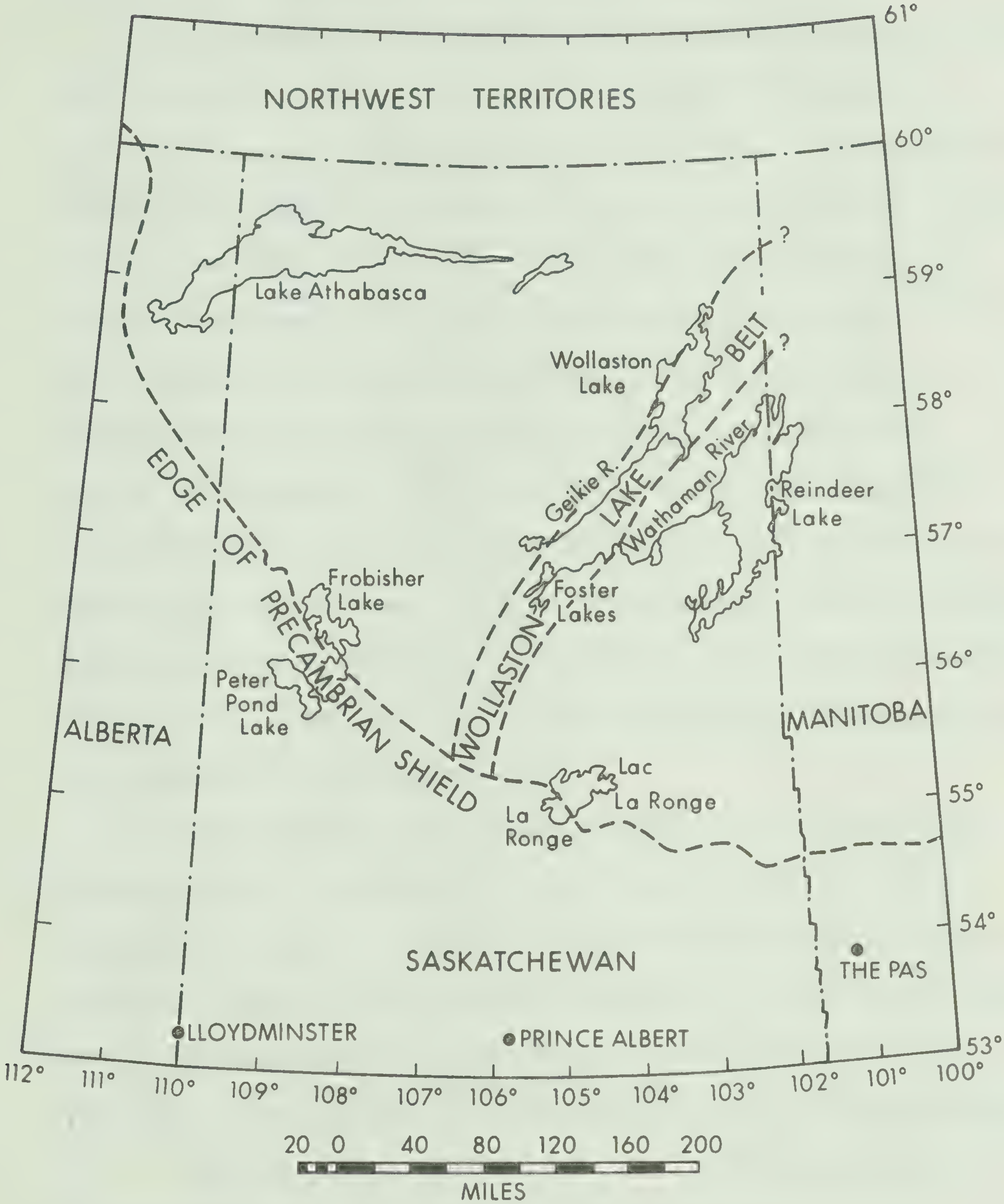

FIGURE 1

LOCATION MAP OF WOLLASTON LAKE FOLD-BELT

(from Rath, 1969)

Local Geology, George Lake Zinc Deposit

The George Lake zinc deposit is found in that portion of the Wollaston Lake trend called the Courtenay Lake-Cairns Lake fold-belt by Money (1968). Karup-Møller (1970) in a detailed study of the belt has renamed it the Compulsion River fold-belt. This belt consists of a steeply dipping sequence of meta-sedimentary rocks. The rock sequence has been subdivided into 6 formations (feldspathic quartzite, quartzite, slate, argillite, arkose and schist). The quartzite hosts the sulphide mineralization which consists of sphalerite, minor galena, pyrite and pyrrhotite. The mineralization occurs as disseminated grains and minor amounts present along fractures. Movement of sulphides into these fractures probably resulted from metamorphic segregation.

Karup-Møller and Brummer (1970) give persuasive evidence that the metals in the mineral deposit are of syngenetic origin, i.e. the precipitation of the sulphides occurred simultaneously with deposition of the host quartzite. The textures of the mineralized sedimentary rocks show that the deposit was later modified by metamorphism.

The geological setting of the individual galena samples won't be given here. Several of the samples were found in boulders of uncertain origin. The geographical locations of the Janice Lake rock specimen, the

George Lake zinc deposit and the discovery sites of the galena samples are given at the end of the chapter (Table 4).

Experimental Results

The writer was initiated into lead isotope work by learning techniques of extracting and purifying lead from galena discovered in the Wollaston Lake area. He then began work on trace lead occurring in whole rocks. The aim was to carry out a study on the average composition of lead extracted from rock samples originating in the Wollaston Lake trend. For this purpose a furnace was built, with the help of Mr. F. Tsong, to extract the lead by volatilization. The first objective was to determine the approximate temperature at which all lead from a whole rock specimen was released. Lead was volatilized and collected for 2 different temperatures (the method is discussed in the Appendix). When run on the mass spectrometer it was noted that the two fractions were significantly different isotopically. Mr. F. Tsong then conducted a heating experiment whereby lead from the rock sample (Janice Lake vicinity) was fractionally removed by distillation at a series of selected temperatures and the isotopic composition of the various lead fractions determined on the mass spectrometer. Concurrently, the writer

commenced an analysis of galena samples found in the general area. The outcome of these two studies proved to be quite interesting and is described below.

Figure (2) illustrates results from the heating experiment and the galena data. Table (2) shows the original galena data along with the additional results for samples E18A, George Lake 9736 and Joannie Showing. The whole rock data won't be repeated here.

A linear trend in the rock lead data is obvious, with the majority of the points fitting a straight line. Cumming et al have suggested that the line is the equivalent of a mineral isochron whereby various mineral phases lose their contained lead at different temperatures. At any particular temperature the lead which is volatilized is a linear combination of contributions from two or more minerals, but which will still plot on a straight line. It is noted that data for 3 temperatures is in disagreement with this premise. However, the join of two of these points is parallel to the main line. The implication here is that there may have been more than one initial lead composition, a reasonable assumption when considering that the rock material is of a sedimentary origin. Since the lines are parallel, it is assumed that there was no mixing between the mineral phases.

Assuming that the radiogenic component of the lead has evolved to the present time t = 0 through the decay of

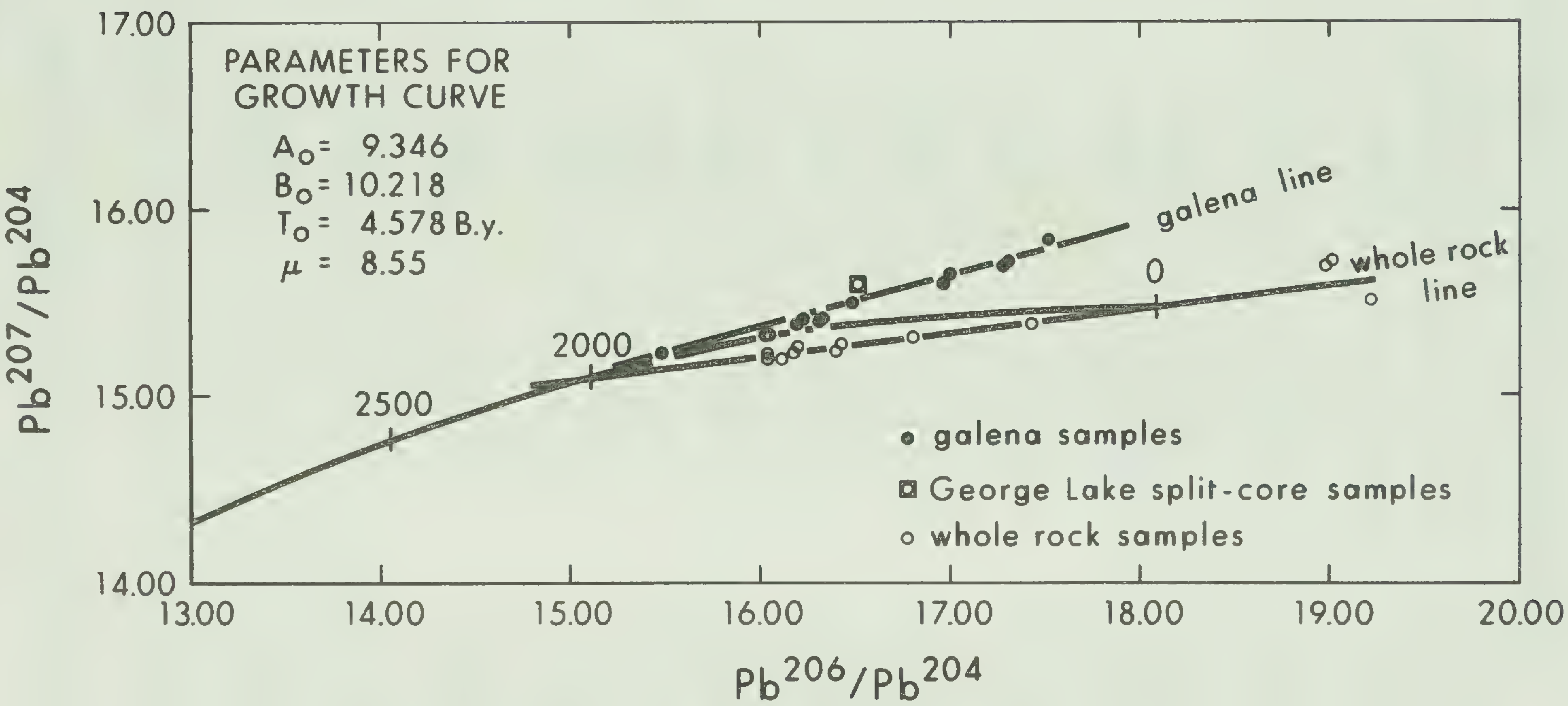

FIGURE 2

LEAD ISOTOPE ANALYSES OF WOLLASTON LAKE FOLD-BELT SPECIMENS

TABLE (2)

LEAD ISOTOPE COMPOSITION OF GALENAS* FROM THE WOLLASTON LAKE FOLD-BELT, SASKATCHEWAN

Sample Name	Pb^{206}/Pb^{204}	Pb^{207}/Pb^{204}	Pb^{208}/Pb^{204}
South of Kaz Lake	15.487 ±0.023	15.226 ±0.023	35.147 ±0.053
Simon Lake	16.201 ±0.022	15.385 ±0.021	35.492 ±0.049
	16.226 ±0.038	15.423 ±0.036	35.646 ±0.085
George Lake 9736	16.334 ±0.037	15.411 ±0.035	35.640 ±0.084
Southwest of George Lake	16.338 ±0.014	15.432 ±0.014	35.641 ±0.031
	16.339 ±0.018	15.430 ±0.018	35.665 ±0.041
George Lake 9748	16.492 ±0.029	15.503 ±0.028	35.849 ±0.065
Wathaman River	16.982 ±0.047	15.624 ±0.044	36.048 ±0.106
	17.011 ±0.019	15.663 ±0.018	36.169 ±0.041
E18A	17.288 ±0.021	15.696 ±0.019	36.290 ±0.044
Marina Showing	17.319 ±0.012	15.744 ±0.011	36.462 ±0.025
Joannie Showing	17.540 ±0.025	15.849 ±0.023	37.404 ±0.054

* George Lake 9736 is a pyrrhotite, Joannie Showing is a chalcopyrite.

uranium, the time t_2 at which the system had an initial uniform lead composition can be calculated from the relationship

$$R \equiv \frac{e^{\lambda' t_2} - e^{\lambda' t_1}}{(e^{\lambda t_2} - e^{\lambda t_1})} = 0.1235 \pm 0.0091 \quad .$$

The slope is determined from the best fitting straight line which is calculated allowing for correlated errors between the two ratios. The constants are given by

$\lambda' = 0.9722 \times 10^{-9}/\text{yr}$

$\lambda = 0.1537 \times 10^{-9}/\text{yr}$

$\alpha = 137.8$

$t_1 = 0$, since the lead was extracted from the rock at the present time.

The value for t_2 is calculated as

$$t_2 = 2040 \pm 135 \text{ m.y.}$$

Money (1968) has reported K-Ar ages of approximately 1750 m.y. for rocks in the area. This implies that the last major metamorphism in the area occurred about 1750 m.y. ago, but was not severe enough to homogenize the lead isotopes.

The μ value for the particular growth curve which intersects the rock line at $t_1 = 0$ or $t_2 = 2040$ m.y. is calculated to be

$$\mu = 8.55 \pm 0.03 \quad .$$

This is the value of μ required to produce the initial lead in the rock at 2040 m.y. and presumably is the value associated with the source from which these rocks originally formed. It is noted that this value is considerably smaller than the value $\mu = 8.79$ for conformable leads as calculated by Cooper et al (1969).

The galena data reported by Cumming et al were also observed to approximate to a straight line, with slope $R = 0.3011 \pm 0.0068$, intersecting the growth curve near the 2040 m.y. date. Assuming a two-stage model for the galena data, the time of the second event is calculated to be

$$t_1 = 2530 \pm 140 \text{ m.y.}$$

This is significant because it indicates that, although the Janice Lake area was involved in the Hudsonian Orogeny some 1700-1800 m.y. ago, crustal material must have been present <u>prior</u> to 2530 m.y. ago at which time the lead was initially emplaced in the rocks. Additional data presented here include samples E18A, George Lake 9736 and

Joannie Showing. They fit the galena line well. The slope of the anomalous lead (galena) line with the inclusion of these 3 additional samples is $R = 0.3009 \pm 0.0082$ which agrees with the original value of 0.3011 ± 0.0068.

Further lead isotope data have also been obtained by the writer for galena in 10 split-core specimens (drill hole number 7) from the George Lake zinc deposit which is located approximately 20 miles south of Wollaston Lake. Results are shown in Table (3). Galena in samples 7-253, 7-254, 7-256, 7-300 and 7-305 occurs in disseminated form. Galena from 7-262, 7-280, 7-297, 7-330 and 7-340 is found in fracture veins. One observes that there is no consistent difference isotopically between the disseminated galena and the more massive vein galena which fill the fractures. It should be noted, however, that samples 7-280 and 7-340 are slightly, but distinctly different isotopically from the rest of the samples. Perhaps these two samples incorporated some radiogenic lead when originally migrating into the fractures. An alternate possibility is that the lead in the George Lake zinc deposit was derived from sources having two slightly different isotopic compositions. The centroid of the George Lake core sample galenas (Pb^{206}/Pb^{204} vs. Pb^{207}/Pb^{204}) is calculated to be

TABLE (3)

LEAD ISOTOPE COMPOSITION OF GEORGE LAKE GALENAS,

DRILL HOLE NUMBER SEVEN

Sample Name	Pb^{206}/Pb^{204}	Pb^{207}/Pb^{204}	Pb^{208}/Pb^{204}
7-340	16.419 ±0.033	15.538 ±0.032	35.979 ±0.075
	16.426 ±0.020	15.562 ±0.019	36.098 ±0.044
7-280	16.420 ±0.024	15.486 ±0.023	35.810 ±0.054
	16.476 ±0.032	15.474 ±0.030	35.825 ±0.070
7-305	16.522 ±0.027	15.579 ±0.026	36.085 ±0.060
7-256	16.549 ±0.029	15.563 ±0.027	36.110 ±0.064
7-262	16.566 ±0.030	15.624 ±0.029	36.220 ±0.067
7-330	16.582 ±0.030	15.644 ±0.028	36.264 ±0.028
7-254	16.593 ±0.026	15.630 ±0.025	36.263 ±0.058
7-297	16.606 ±0.028	15.676 ±0.026	36.367 ±0.061
7-300	16.614 ±0.021	15.660 ±0.019	36.333 ±0.045
7-253	16.622 ±0.018	15.654 ±0.017	36.345 ±0.039

Pb^{206}/Pb^{204}	Pb^{207}/Pb^{204}
16.540 ±0.011	15.599 ±0.010

From Figure (2), the George Lake core sample galenas are seen to depart slightly from the galena lead line and have probably had a slightly different origin than the others.

Sinha (1970) has reported lead isotope data for 2 galena samples in the Wollaston Lake belt. The data (normalized to absolute ratios using CIT shelf lead) is quoted here.

Sample Name	Pb^{206}/Pb^{204}	Pb^{207}/Pb^{204}	Pb^{208}/Pb^{204}
Compulsion River	16.55	15.63	36.47
	16.55	15.63	36.44
	16.54	15.63	36.47
Falconbridge	16.47	15.40	36.89

The data listed here do not coincide with any data obtained by the writer for galena samples found in the Wollaston Lake trend. Sinha (1970) mentions that both galenas are found in boulders which may be unrelated to Churchill Province rocks, although the writer is of the understanding that the sample "Compulsion River" as listed by Sinha may correspond to the sample "Southwest of George Lake" as given by the writer.

TABLE (4)

LOCATIONS OF WOLLASTON LAKE TREND SAMPLES

Sample Name	Location
Janice Lake	104°56' W, 56°50' N
George Lake 7253-7340	103°47' W, 57°28' N
George Lake 9736	-
George Lake 9748	-
George Lake 86087	-
Southwest of George Lake	103°51' W, 57°27' N
Simon Lake	103°39' W, 57°41' N
South of Kaz Lake	104°57' W, 56°53' N
Wathaman River	104°25' W, 56°57' N
Marina Showing	104°09' W, 57°27' N
Joannie Showing	103°31' W, 57°36' N
E18A	103°58' W, 57°34' N

CHAPTER III

A LEAD MODEL STUDY OF THE QUEMONT DEPOSIT

Geology

The Quemont mine is located at Noranda, Quebec (Fig. 3). Regional geology has been compiled by Dugas and Gilbert (1953). Campbell (1962 and 1963) has described the mine geology on the basis of field studies and earlier reports by Taylor (1953, 1957), Scott (1948) and others. The following geological summary is founded mainly on his descriptions.

Noranda lies between the Cadillac-Bouzan and Porcupine-Destor fault zones. The Cadillac-Bouzan fault zone separates Timiskaming-type sediments in the south from Keewatin-type volcanics to the north. A series of stocks, sills and dikes have been mapped in the area. The Horne Creek fault at Noranda divides the Quemont and Horne mines.

The Quemont mine is located in volcanics consisting mainly of rhyolite porphyries, breccias and tuffs. Ore occurs in the rhyolite breccias. Porphyritic rhyolite overlies the ore. The porphyritic rhyolite and rhyolite breccia are folded into a westerly plunging anticline. Further crossfolding has resulted in a domal capping of the porphyritic rhyolite over the ore zones. The dome is abruptly truncated by the Horne Creek fault.

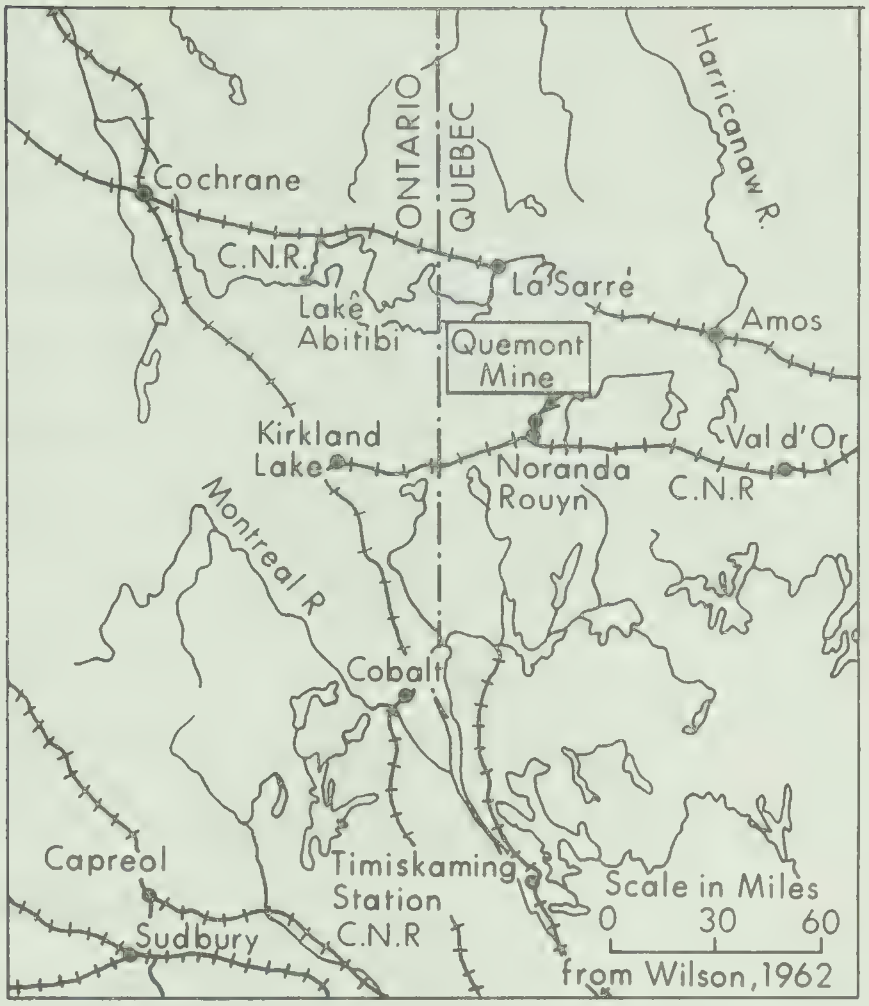

FIGURE 3

LOCATION MAP, QUEMONT MINE

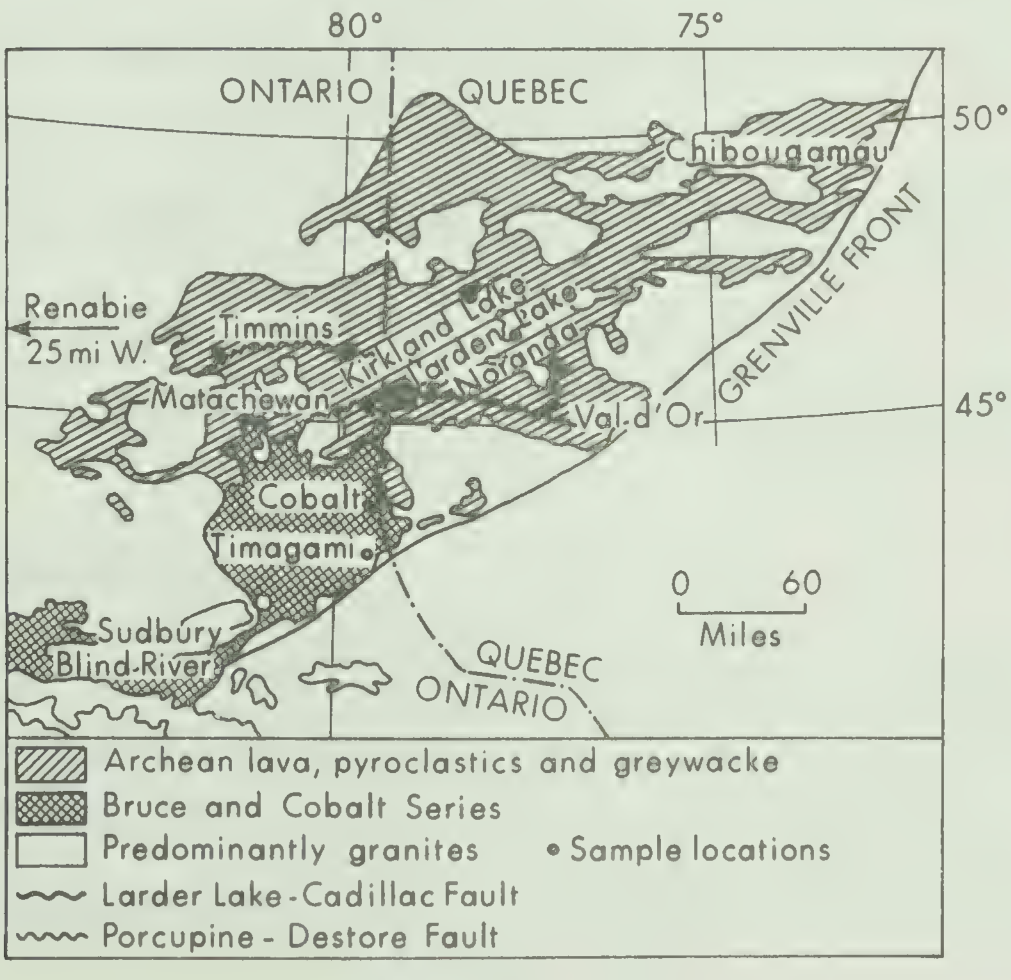

FIGURE 4

GENERAL GEOLOGY, COBALT-NORANDA AREA
(from Kanasewich and Farquhar, 1965)

The ore at Quemont occurs as massive and disseminated sulphides. Predominant minerals are pyrite, pyrrhotite, sphalerite, chalcopyrite and magnetite. Pyrite and pyrrhotite are the dominant sulphides, constituting about 87 per cent by weight of the ore minerals. Sphalerite and chalcopyrite account for the remaining 13 per cent. Galena is found in small quantities in one part of the mine.

Campbell (with Ryznar et al, 1967) has proposed the following series of events, with corresponding dates, for the Quemont mine area:

"1. Deposition of non-porphyritic rhyolite breccia and rhyolites
2. Deposition of porphyritic rhyolite and andesites
3. Folding and fracturing of volcanic rocks
4. Emplacement of sulphide ores - 3250 m.y.
5. Intrusion of diorite
6. Granitic intrusions (and rhyolite dikes) - 2450 m.y.
7. Diabase dikes - 1200-1700 m.y."

Numbers quoted are lead model and K-Ar radiometric dates.

Experimental results

A lead isotope analysis was made on 8 sulphide samples from the Quemont mine with the anticipation that a lead model study might furnish new information on its geological history. Results are given in Table (5).

TABLE (5)

QUEMONT MINE - UNIVERSITY OF ALBERTA RESULTS

Sample name	Pb^{206}/Pb^{204}	Pb^{207}/Pb^{204}	Pb^{208}/Pb^{204}
Q 15 Pyrrhotite	13.907 ±0.012	14.595 ±0.013	33.690 ±0.029
Q 64 Chalcopyrite	13.908 ±0.007	14.642 ±0.008	33.871 ±0.018
Pyrrhotite (elev. 9825')	14.877 ±0.017	14.848 ±0.017	34.808 ±0.040
Pyrite (elev. 9825')	14.898 ±0.045	14.807 ±0.045	34.742 ±0.107
Q 15 Pyrite	14.937 ±0.046	14.809 ±0.046	35.116 ±0.109
Q 15 Pyrite	15.069 ±0.026	14.889 ±0.026	35.326 ±0.061
Q 45 Pyrrhotite	15.953 ±0.047	15.051 ±0.045	36.126 ±0.108
Chalcopyrite 12-1803	18.099 ±0.023	15.540 ±0.020	39.915 ±0.050
Galena (B.T. Quemont)	21.304 ±0.023	16.188 ±0.017	44.634 ±0.048

Lead isotope results obtained by Kanasewich and Farquhar (1965) for galenas in the Cobalt-Noranda area are of interest for this work. These results are given in Table (6).

A plot of the Quemont and Cobalt-Noranda data as a Pb^{207}/Pb^{204} vs. Pb^{206}/Pb^{204} graph is illustrated in Figure (5). The primary growth (Cooper et al, 1969) is also included.

<u>Interpretation</u>

It is apparent that the Quemont mine data nicely approximate an anomalous lead line on a Pb^{207}/Pb^{204} vs. Pb^{206}/Pb^{204} plot. The slope of the line is given by

$$R = .2117 \pm .0028 \quad .$$

It is seen from Figure (5) that the Quemont mine and Cobalt-Noranda anomalous lead lines have slightly different intersections at the primary growth curve ($\mu = 8.79$). Kanasewich and Farquhar (1965) recognized the Cobalt-Noranda galenas as being mixtures of single-stage galenas having two distinct periods of mineralization - at 3200 ± 150 m.y. and 2300 ± 150 m.y. If their data are normalized to absolute values according to Cooper et al (1969), these two dates become 3360 ± 70 m.y. and 2140 ± 70 m.y. The errors encompass experimental

TABLE (3)

COBALT-NORANDA GALENAS (KANASEWICH AND FARQUHAR,1965)*

Sample name	Pb^{206}/Pb^{204}	Pb^{207}/Pb^{204}	Pb^{208}/Pb^{204}
Golden Manitou Mine, Val d'Or, Que.	13.227 ±0.013	14.408 ±0.014	32.993 ±0.033
Barvue Mine, Que.	13.226 ±0.013	14.428 ±0.014	33.032 ±0.033
Renabie Mine, Ont.	13.286 ±0.013	14.398 ±0.014	32.993 ±0.033
Kerr Addison Mine, Ont.	13.663 ±0.014	14.616 ±0.015	33.358 ±0.033
Lake Shore Mine, Kirkland Lake, Ont.	14.220 ±0.014	14.824 ±0.015	33.744 ±0.034
Kerr Lake Mine, Coleman Twp., Ont.	14.696 ±0.015	15.091 ±0.015	34.288 ±0.034
Lawson Mine, Cobalt, Ont.	14.706 ±0.015	15.101 ±0.015	34.298 ±0.034
Cobalt, Ont.	14.865 ±0.015	15.150 ±0.015	34.426 ±0.034
Quemont Mine, Que. 4 Lvl.	20.634 ±0.040	16.074 ±0.040	44.533 ±0.090
Quemont Mine, Que. 12 Lvl.	21.092 ±0.050	16.133 ±0.050	43.339 ±0.110
	21.142 ±0.060	16.114 ±0.060	43.339 ±0.130

* Data corrected to absolute abundances of Broken Hill #1 according to Cooper et al (1969).

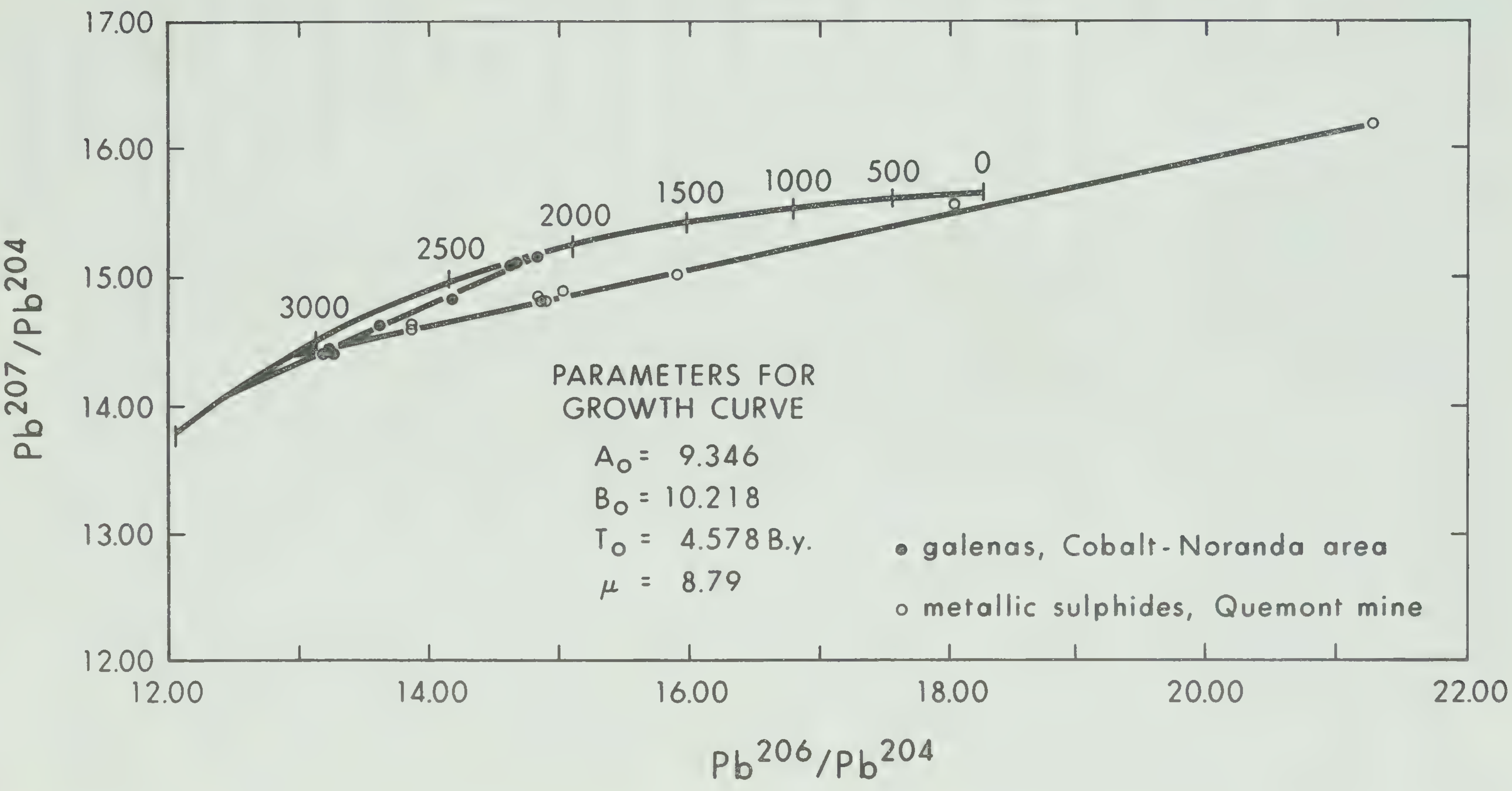

FIGURE 5

LEAD ISOTOPE ANALYSES OF SULPHIDES, QUEMONT MINE AND COBALT-NORANDA GALENAS

uncertainties in the isotope measurements only. The Quemont anomalous lead line intersects the primary growth curve at 3050 ± 50 m.y. Furthermore, the Quemont mine (galena) data listed by Kanasewich and Farquhar, which are older University of Toronto data, agree quite well with the galena data obtained by the writer at the University of Alberta.

A puzzling aspect of the Quemont data is the fact that the anomalous lead line passes very close to the present day end of the growth curve. It was initially suspected that the iron sulphide separates might contain some admixtures of uranium rich accessory mineral. However x-ray diffraction films taken by Mr. M. Gold at the Department of Geology, University of Alberta failed to indicate the presence of significant contamination. It should be noted though, that as much as 5 per cent admixture might have been present and remained undetected. Such a contamination of the iron sulphides would not account for the fact that the galena sample lies on the same straight line and it is therefore concluded that the data represents a true anomalous lead line and may be interpreted in terms of a simple model. Since a two-stage model interpretation would require a mineralizing event at essentially zero time for which there is no geologic evidence, it is apparent that a more complex model is necessary.

A modified three-stage model for the lead in the galena and other sulphides in the Quemont deposit is proposed here. It is suggested that the history of lead at Quemont is marked by three stages of mineralization given by t_1, t_2 and t_3 where

t_1 is the time of ordinary lead mineralization;

t_2 is the time of uranium-thorium mineralization;

t_3 is the time of anomalous lead mineralization during which radiogenic lead, having developed between t_2 and t_3, is added to the ordinary lead.

Ulrych and Russell (1964) adopted such a model in interpretating the history of the Sudbury leads. The relevant equations for this model are

$$x_3 = a_o + \mu_1 \left(e^{\lambda t_o} - e^{\lambda t_1}\right) + \mu_3 \left(e^{\lambda t_2} - e^{\lambda t_3}\right)$$

$$y_3 = b_o + \frac{\mu_1}{137.8} \left(e^{\lambda' t_o} - e^{\lambda' t_1}\right) + \frac{\mu_3}{137.8} \left(e^{\lambda' t_2} - e^{\lambda' t_3}\right)$$

$$z_3 = c_o + W_1 \left(e^{\lambda'' t_o} - e^{\lambda'' t_1}\right) + W_3 \left(e^{\lambda'' t_2} - e^{\lambda'' t_3}\right) .$$

The slope of the anomalous lead line is given by equation (21) (Chapter I)

$$R \equiv \frac{y_3 - y_1}{x_3 - x_1} = \frac{\left(e^{\lambda' t_2} - e^{\lambda' t_3}\right)}{137.8\left(e^{\lambda t_2} - e^{\lambda t_3}\right)} .$$

The time, t_1, of ordinary lead mineralization is taken to be 3050 ± 50 m.y. This age indicates the first period of lead mineralization and is slightly discrepant with first age of mineralization calculated by Kanasewich and Farquhar (1965) for the Cobalt-Noranda galenas.

As mentioned previously, equation (21) cannot be solved explicitly for both t_2 and t_3. An independent estimate for either t_2 or t_3 is required. An obvious choice for t_2 would be a date coinciding with the Kenoran Orogeny in the Superior province.

The value 2500 ± 100 m.y. for the second period of lead mineralization of the Cobalt-Noranda galenas is chosen for t_2 in this work. Numerous K-Ar ages centered around 2500 are listed in Geological Survey of Canada Map 1256A (Isotopic Age Map of Canada compiled by Wanless, 1969) representing granitic intrusions in the Superior geological province. Campbell (1962) has quoted a K-Ar age (determined by Dr. H. Baadsgaard at the University of Alberta) of 2440 ± 200 m.y. for diorite at Quemont. He interprets this age as representing the last thermal event in the area (probably associated with the introduction of granites). This date may, in fact, represent the culmination of the Kenoran Orogeny in the immediate vicinity of Noranda. Remobilization of the existing sulphides might have taken place, but it is suggested

that the lead was <u>originally</u> deposited in a low U-Th environment and little change in the isotopic composition of the lead was effected.

It is plausible that uranium-thorium mineralization was associated with the intrusion of granites during the Kenoran Orogeny (which may have spanned several hundred million years as suggested by Ozard, 1970). In brief, the date t_2 is thought to depict uranium-thorium mineralization during the Kenoran Orogeny and is taken to be 2500 ± 100 m.y.

If one accepts t_2 to be 2500 m.y., then from equation (21) the value for t_3, the time of anomalous lead mineralization, is calculated to be 1050 ± 100 m.y. It is interesting to note that this date coincides with an accepted date of 1000 ± 100 m.y. (e.g. Zartman and Wasserburg, 1969) for the Grenville Orogeny. Since Noranda lies some 50 miles from the Grenville Front, a direct correlation between these two ages must be viewed with some skepticism. Nevertheless, a mechanism related to the Grenville Orogeny whereby anomalous lead is added at 1050 m.y. to the older 3050 m.y. ordinary lead is proposed.

In recent years, researchers such as Grant (1964), Steiger and Wasserburg (1969) and Ozard (1970) have demonstrated that old Superior rocks near the Grenville

Front have been altered by metamorphism approximately 1000 m.y. ago during the Grenville Orogeny. Attention was focused on the fact that radiogenic lead is quite easily mobilized during metamorphic events. This is easily explained when noting that uranium and thorium frequently occur interstitially in accessory minerals. The lead generated by radioactive decay is not compatible with the host lattice. Ozard (1970) has surmised that lead in the Vogt-Hobbs area of Ontario has migrated over a distance of several miles. If one concedes that radiogenic lead may migrate during metamorphism, then given a channelway, perhaps this migration can extend for a considerable distance. Kanasewich and Farquhar (1965) have suggested that the Cadillac-Boizan and Porcupine-Destor fault zones may have served as channelways for mineral-bearing fluids during the periods of lead mineralization in the Cobalt-Noranda area. It is conceivable that these same fault zones served as channelways for the remobilized radiogenic lead at 1050 m.y. Campbell (1962) has suggested that the Cadillac and Porcupine fault zones might be genetically related to the Grenville Front. The radiogenic lead, having migrated along these faults, would then enter the host rock through secondary faults (as the Horne Creek fault) and fissures. This radiogenic lead is added to the older lead already existing in the Quemont ore deposit.

CHAPTER IV

A LEAD ISOTOPE INVESTIGATION OF THE BIG LEDGE ZINC DEPOSIT

Geology

The Big Ledge zinc deposit is located 36 miles south of Revelstoke, British Columbia (Figure 6) and is one of a number of lead-zinc deposits in the southeastern part of British Columbia. The geology of the deposit and surrounding area has been described by Raham (1967), his report forming the basis for much of the following summary of the relevant geology.

The Big Ledge zinc deposit occurs in the Shuswap metamorphic complex which consists of sillimanite grade marbles, quartzites and gneisses in this area. The rocks are of Lower Palaeozoic or Cambrian age and have been metamorphosed in Upper Cretaceous time. The ore deposit is stratabound, enclosed entirely within the Ledge Unit. Three periods of deformation have altered rock units in the vicinity of Big Ledge, resulting in an east-trending synform modified by two later periods of deformation. The first deformation period resulted in the formation of a large overturned fold. Later, smaller scale isoclinal folds were produced, generally coaxial with the large fold. It is probable that during this folding period

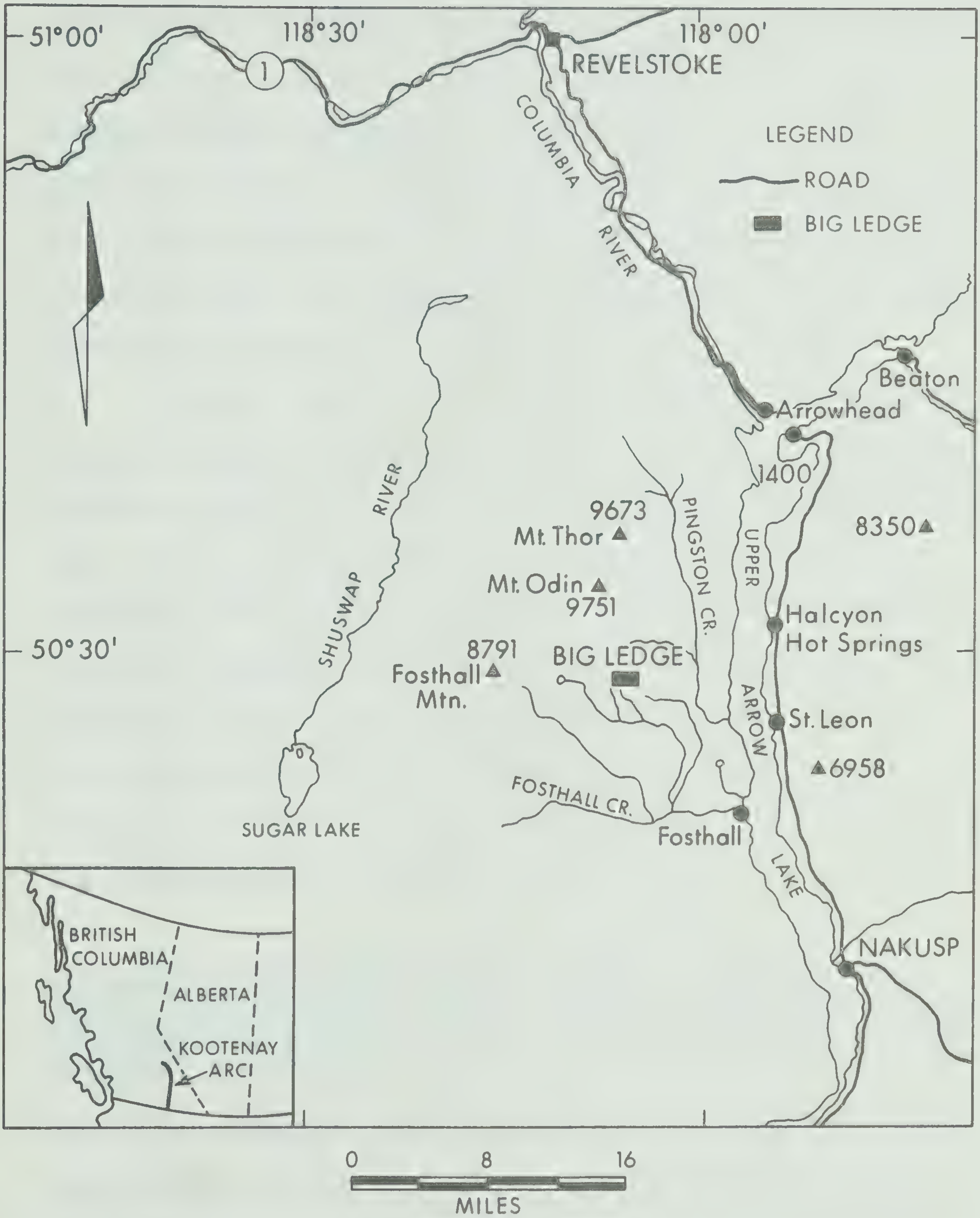

FIGURE 6

LOCATION MAP, BIG LEDGE ZINC DEPOSIT

(from Raham, 1967)

the Ledge Unit was deformed into a drag or secondary fold. Finally, gentle warps were produced in the bedding. Dates for the last periods of major metamorphism have been obtained by the K-Ar method. Reesor (1963, 1964, 1965, 1966) has shown that the Shuswap terrain has experienced major metamorphic events during late Cretaceous and early Tertiary time. In particular, K-Ar dates of 64 and 89 m.y. have been obtained from Mount Oden, near Big Ledge.

Besides zinc which is the only economic mineral, other sulphides at Big Ledge consist of pyrite, pyrrhotite, sphalerite and traces of galena, chalcopyrite and marcasite. The sulphide deposit has been formed by replacement of calcerous and non-calcerous horizons, deposition in fractures and deposition in breccia zones. The origin of the solutions which formed the orebody is unknown. In fact, there is controversy as to whether the orebody is post- or pre-metamorphism. Raham (1967) cites evidence that the Big Ledge deposit is post-metamorphism:

> "... the crosscutting nature of the sulphides, brecciation, fracture filling, veining, a general lack of conclusive deformational textures, numerous occurrences of euhedral sulphides and the presence of sulphides in any and every rock type ..."

It could be argued, however, that all of Raham's criteria might simply represent remobilization of material already in place prior to the metamorphism. Muraro (1966) believes that other Shuswap deposits such as Wigwam and Ruddock Creek

existed in their respective host rocks before major folding and metamorphism.

Experimental Results

Lead isotope results for 17 Big Ledge samples analyzed at the University of Alberta are given in Table (7). The samples were comprised of galenas, pyrites and pyrrhotites.

Interpretation of Results

It is evident that the lead isotope composition of the Big Ledge samples is quite uniform. The centroid (average) of the data on a Pb^{206}/Pb^{204} vs. Pb^{207}/Pb^{204} plot is given by

Pb^{206}/Pb^{204}	Pb^{207}/Pb^{204}
19.443 ±0.008	15.802 ±0.007

Sinclair (1964) observed such a uniformity for individual deposits in a study of leads from the Kootenay Arc (a belt of metamorphic rocks extending from northern Washington to north of Revelstoke, B.C.). He found that thermally metamorphosed galena samples from the Jersey Mine had identical isotopic composition to other Jersey Mine lead. In addition, galena from a small vein in the Reeves

TABLE (7)

BIG LEDGE SULPHIDES

Sample name	Sulphide type	Pb^{206}/Pb^{204}	Pb^{207}/Pb^{204}	Pb^{208}/Pb^{204}
R 1	galena	19.438 ±0.029	15.784 ±0.023	39.880 ±0.060
R 2	galena	19.501 ±0.041	15.866 ±0.033	40.183 ±0.085
R 2	galena	19.490 ±0.033	15.878 ±0.027	40.196 ±0.068
R 104	galena	19.505 ±0.037	15.859 ±0.030	40.121 ±0.077
R 104	galena	19.523 ±0.029	15.876 ±0.024	40.160 ±0.061
R 122	galena	19.452 ±0.031	15.789 ±0.026	39.946 ±0.065
R 365	galena	19.419 ±0.047	15.806 ±0.039	40.025 ±0.101
R 468	galena	19.389 ±0.035	15.760 ±0.029	39.837 ±0.072
R 72	pyrite	19.418 ±0.046	15.780 ±0.037	39.869 ±0.095
R 319	pyrite	19.373 ±0.047	15.712 ±0.039	39.681 ±0.098
R 411	pyrite	19.457 ±0.069	15.764 ±0.056	39.798 ±0.144
R 413	pyrite	19.389 ±0.046	15.771 ±0.038	39.887 ±0.098
R 423	pyrite	19.449 ±0.031	15.832 ±0.025	40.044 ±0.064

TABLE (7) (cont'd)

BIG LEDGE SULPHIDES

Sample name	Sulphide type	Pb^{206}/Pb^{204}	Pb^{207}/Pb^{204}	Pb^{208}/Pb^{204}
R 449	pyrite	19.333 ±0.036	15.744 ±0.029	39.742 ±0.075
R 468	pyrite	19.408 ±0.059	15.773 ±0.048	39.873 ±0.123
R 133	pyrrhotite	19.395 ±0.037	15.775 ±0.030	39.764 ±0.077
R 319	pyrrhotite	19.432 ±0.038	15.790 ±0.031	39.920 ±0.076
R 438	pyrrhotite	19.470 ±0.029	15.778 ±0.023	39.887 ±0.060
R 468	pyrrhotite	19.435 ±0.060	15.764 ±0.049	39.806 ±0.124

McDonald Mine was identical in composition to the massive parts of the orebody. Apparently a homogeneity of isotopic composition does not necessarily indicate whether or not metamorphism of an orebody has taken place. Bearing this in mind when considering the Big Ledge samples, the lead isotope results obtained here apparently do not give new evidence on the question of the deposit being post- or pre-metamorphism.

Along with isotope data for leads from the Kootenay Arc itself, Sinclair (1964) also reported lead isotope data for deposits in the adjacent Shuswap terrain (i.e. the Wigwam, Cottonbelt and Ruddock Creek deposits). The Wigwam deposit in particular is located only some 30 miles from the Big Ledge deposit. It is instructive to view the Big Ledge data in light of Sinclair's results.

Sinclair showed that a suite of lead samples from the Kootenay Arc (and from the Shuswap complex) very closely defined an anomalous lead line in a Pb^{206}/Pb^{204} vs. Pb^{207}/Pb^{204} plot. His data will not be retabulated here (see Sinclair, 1966). However, a plot of the Kootenay Arc data along with the Big Ledge data is illustrated in Figure (7). The Big Ledge data are seen to plot very closely to the Kootenay Arc anomalous lead line. Sinclair noted, in addition, that the calculated Th/U ratios for the various deposits are quite uniform. He suggested that this may indicate that the source of the leads for the

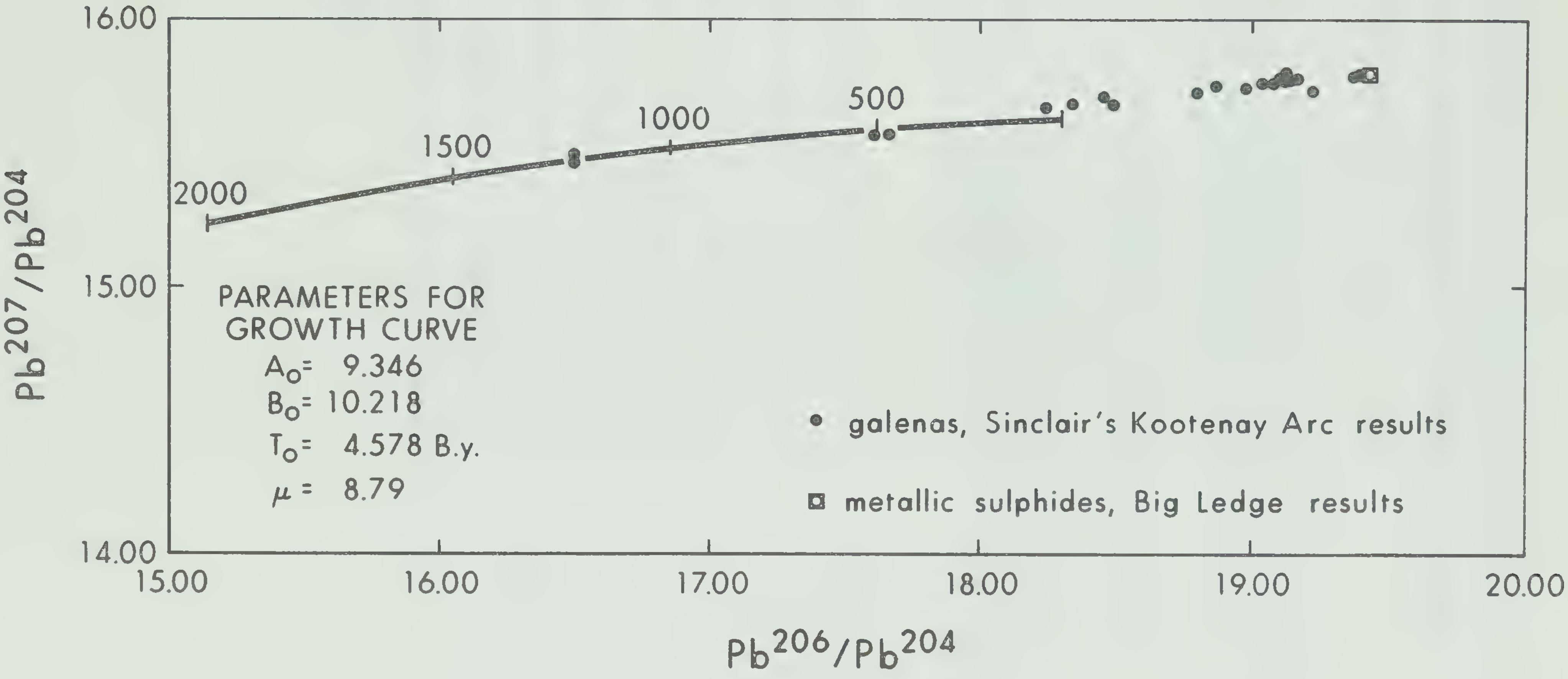

FIGURE 7

LEAD ISOTOPE ANALYSES, KOOTENAY ARC AND BIG LEDGE RESULTS

entire Kootenay district was quite uniform. Sinclair (1966) has postulated the following sequence of events for the Kootenay Arc leads:

"1. Introduction of U and Th into a closed system in the upper crust about 1700 m.y. age. This closed system, the immediate source of Kootenay Arc leads may have been Lower Purcell Strata.

2. Introduction of Sullivan-type leads into the crustal source of Kootenay Arc leads about 1340 m.y. ago.

3. Mixing of Sullivan-type lead and radiogenic lead formed from radioactive decay of U and Th, by local melting and eventual production of hydrothermal fluids during Coast Range Orogeny, probably about Middle Jurassic time."

The indication is that the few leads analyzed from the Shuswap metamorphic complex, including lead from the Big Ledge deposit, have had a history similar to the Kootenay Arc leads. Furthermore the uniformity of the lead isotope composition suggests that the Jurassic-Cretaceous metamorphism must have been severe to so thoroughly homogenize the lead present in this deposit. The lead has probably been derived from the same source as that of the Kootenay Arc leads.

CHAPTER V

SUMMARY AND CONCLUSIONS

The primary aims of this thesis have been to report new lead isotope data obtained by the writer for sulphide specimens from the Wollaston Lake fold-belt area, the Big Ledge zinc deposit and the Quemont mine and, further, to suggest interpretations of this data which, it is hoped help to elucidate the geological histories of the deposits and their environments. To this end, the writer had to first learn the techniques involved in the chemical processing and general mass spectrometry procedures necessary to achieve reliable data. Data was obtained on a solid source mass spectrometer equipped with a new digital recording system and processed by an IBM 360 computer by reduction techniques described by Cumming et al (1971).

The results of a heating experiment conducted on a whole rock specimen from the Wollaston Lake trend showed that the lead in the rock was distributed inhomogeneously. When fractionally removed by incremental heating, the isotopic compositions of the lead fractions varied in a well defined manner, with most of the data fitting on a straight line (Cumming et al, 1970). Calculations indicated that the rock sample became a closed system with respect to lead 2040 ± 135 m.y. ago, considerably before

[illegible]

the last major thermal event in the area indicated by a K-Ar age of 1750 m.y. The value for μ (the present day U^{238}/Pb^{204} value) required to produce the rock lead 2040 m.y. ago is calculated to be given by $\mu = 8.55 \pm 0.03$. The galena data for samples in the vicinity indicates that the lead in these rocks was initially emplaced 2530 ± 140 m.y., necessitating the presence of crustal material in the area prior to this time.

The isotopic composition of lead in the Big Ledge zinc deposit was shown to be very uniform, with the data lying along the Kootenay Arc anomalous lead line of Sinclair (1966). The lead in the deposit, which is located in the Shuswap metamorphic complex, appears to have been derived from the same source as the Kootenay Arc leads and has apparently experienced a similar history. The uniformity of the lead isotope composition suggests that the Jurassic-Cretaceous metamorphism must have been severe to so thoroughly homogenize the lead ratios in this large deposit.

Lead extracted from metallic sulphide samples of the Quemont mine was seen to have isotopic compositions fitting closely to an anomalous lead line. A three stage model is proposed to account for the lead isotope abundances in the deposit. Ordinary lead mineralization in the Quemont mine area occurred at $t_1 = 3050 \pm 50$ m.y.,

representing the initial emplacement of lead in crustal rocks. If an age for uranium and thorium emplacement is chosen as $t_2 = 2500 + 100$ m.y., then the time t_3 of anomalous lead mineralization is calculated to be $t_3 = 1050 \pm 100$ m.y. This value represents the time at which radiogenic lead, having developed from 2500 m.y. is mixed with the older ordinary lead. It is observed that the value $t_3 = 1050 + 100$ m.y. agrees with a generally accepted value for the Grenville Orogeny.

APPENDIX

LEAD EXTRACTION AND PURIFICATION PROCEDURES

For purposes of chemical processing, the samples were grouped into three categories- galenas (PbS), other sulphide minerals and whole rocks. The techniques in extracting and purifying the lead are somewhat different for each group. Lead is extracted by acid leaching or volatilization and purified by either the dithizone method or an ion exchange process (or a combination of both methods).

Dithizone method

The dithizone technique of extracting lead has been described by Tilton et al (1955), Maynes and McBryde (1957), Sandel (1959) and others. The following discussion of the dithizone procedure is a review based on the references cited above.

Dithizone (Diphenylthiocarbazone) is a solid organic compound which dissolves readily in most organic solvents. When an immiscible organic solution of dithizone is shaken with an aqueous solution of a reacting heavy metal a colored dithizonate complex is formed, the color depending on the metal present. Although dithizone reacts with about twenty metals other than lead, adjustment of the pH of the solution to be extracted and addition of a complex - forming

agent to tie up other reacting metals permits a separation specifically for lead. Ammonium citrate and potassium cyanide are frequently used as such agents. Citrate prevents precipitation of metal hydroxides and cyanide forms complexes (with such metals as iron) greatly reducing the amount of interfering metal reacting with dithizone. The cyanide does not prevent lead from reacting with the dithizone. A common technique which works in the case of a low concentration of reacting metals is to first extract lead <u>and</u> other reacting metals. Then the dithizonate complex is separated from the original solution and shaken with dilute acid, releasing the lead and leaving "contaminant" metals still complexed with the dithizone.

If contaminant reacting metals are present in large amounts then by mass action considerable quantities of contaminant metal will react with the dithizone, necessitating a preliminary purification stage. An initial ion-exchange separation of lead will adequately remove concentrations of contaminant metal.

Ion-exchange method

Kraus and Nelson (1955) studied the adsorbability by Dowex-1 ion-exchange resin in various HCl concentrations of different elements. They observed that lead was weakly adsorbed over a considerable range of acidity, with minimum adsorption at approximately O M and 8 M. Maximum adsorption

occurred at approximately 1.5 M. Further studies indicated that whereas lead is adsorbed from 1.5 M HCl, the alkaline earth metals, copper, iron, tin and thallium are not. This suggested that lead could be separated from many metals by adsorption on Dowex-1 resin from 1.5 M HCl and desorption by de-ionized (neutral) water. The ion-exchange method employed in this work is a modification of the method outlined by Catanzaro and Gast (1962).

In order to achieve a good "run" on the mass spectrometer purity of sample is critical. For example, traces of iron impurity will kill a run. The chemistry procedures adopted in this work gave adequate or better runs on the mass spectrometer and will be described in detail.

<u>Reagents used</u>

Triple-distilled water (3D water): used in the preparation of other reagents.

Ammonium citrate: a 30% solution in 2% NH_4OH is prepared, extracted with dithizone and washed with chloroform.

Potassium cyanide: a 4% solution in 2% NH_4OH is prepared, extracted with dithizone and washed with chloroform.

Ammonium hydroxide: obtained from The British Drug Houses Ltd. (BDH) - Aristar grade, with maximum limit of Pb impurity quoted at 0.0000001 %.

Chloroform: reagent grade chloroform is washed three times with dilute HCl then five times with 3D water.

Dithizone: a 0.01% stock solution in chloroform is washed three times with 3 M HCl and five times with 3D water; this solution extracts about 40 μg.of lead per ml.; the dithizone should be stored in a refrigerator since heat, light decompose it.

Nitric acid: BDH - Aristar grade.

Hydrochloric acid: BDH - Aristar grade.

Bromine: BDH - Aristar grade.

Hydrogen sulphide:

Dowex 1 - X8 resin: a strongly basic, anion exchange resin (ionic form Cl^-), 100-200 mesh from Baker.

To keep contamination to a minimum all the glassware (beakers, separating funnels, centrifuge tubes etc.) were previously cleaned in hot, concentrated nitric acid and rinsed first with 1D water and then with 2D water.

Extraction of lead from galenas

(1) Put a crystal or two of galena in a small beaker and add 5 ml. of concentrated HNO_3. Evaporate to dryness. Take up evaporate in approximately 10 ml. of 3D water.

(2) Decant solution into a 125 ml. separatory funnel. Bring the pH of the solution to 9-10 by adding a few drops of concentrated NH_4OH. Add 10 ml. of ammonium citrate and 5 ml. of potassium cyanide.

(3) Add dithizone to the separatory funnel and shake. The dithizone will turn cinnabar red. Remember that 1 ml. of the stock solution will extract 40 µg. of lead.

(4) Carefully drain the lead-dithizonate complex (drop by drop) into a 60 ml. separatory funnel, making sure not to include a drop of the citrate-cyanide solution containing iron and other contaminants. Add 20 ml. of 3D water and gently shake. Drain the red dithizonate complex into a 5 ml. beaker. Rinse the 60 ml. separatory funnel with 3D water.

(5) Pour the dithizonate back into the 60 ml. separatory funnel. Add 1-1.5 ml. of 2% HNO_3 to back - extract the lead. The lead is now present in nitrate form in the clear solution above the green dithizone at the bottom of the separatory funnel.

(6) Drain away the green dithizone. Wash the remaining solution several times with 5-10 ml. of chloroform, draining off the chloroform each time.

(7) Add the lead nitrate solution to the (cleaned) 125 ml. separatory funnel and repeat steps (2) to (6).

(8) Pour the lead nitrate into a 2 ml. centrifuge tube and add several drops of dilute NH_4OH to bring the pH to 4-5

(9) Bubble the solution with H_2S to precipitate the lead as PbS. Centrifuge. The lead sulphide settles as a sludge at the bottom of the precipitate tube.

The sample is now ready to be loaded on a filament as PbS in an ammonium nitrate flux.

If the galena is disseminated and occurs with pyrite or pyrrhotite, quite often the galena will tend to enclose the pyrite (or pyrrhotite) crystals and grains. The dithizone procedure alone is not always successful for such a case. A preliminary precipitation of lead as lead iodide (PbI) before a dithizone extraction helps to eliminate some of the iron contamination. The procedure here is to dissolve the galena in HNO_3, take the solution to dryness and add 5-10 ml. of 10% potassium iodide. Lead iodide is formed (a dense yellow precipitate). Decant the liquid and wash the lead iodide with acetone. Then proceed with the dithizone extraction.

If the galena occurs only in very minor amounts along with other metal sulphides an ion-exchange purification is advisable.

Extraction of lead from sulphide minerals

Metallic sulphides such as pyrites, pyrrhotites and chalcopyrites nearly always contain at least microgram traces of lead. The relatively large amount of iron present can be chemically separated from the lead by employment of an ion-exchange process.

(1) Place 1 gm of sulphide in a vycor crucible. Add 15 ml. of 50% HNO_3 and a few drops of bromine. Gently evaporate to dryness on a hot plate (this may take 12 hrs.).

(2) Add 4 ml. of concentrated HCl. Evaporate to dryness. Repeat this step with 2 ml. of concentrated HCl.

(3) Add 30 ml. of 1.5 M HCl to dissolve the evaporate.

(4) Filter, then pour this solution into an ion-exchange column which is packed with Dowex 1-X8 resin settled in 1.5 M HCl. The particular columns used were approximately 1 cm. x 30 cm. with a 100 ml. capacity reservoir.

(5) Pass the 1.5 M solution through the column. Discard the eluate. Wash the reservoir twice with 15 ml. of 1.5 M HCl, allowing the HCl to pass through the column. This will remove traces of solution adhering by capillary action.

(6) Elute the columns with 70 ml. of 1.5 M HCl.

(7) Strip the lead from the resin by adding 60 ml. of 3D water. The first 10 ml. of eluate can be discarded.

(8) Evaporate the solution to dryness.

(9) Convert the evaporate to nitrate form by adding 2 ml. of concentrated HNO_3 and again evaporating to dryness. Take up the evaporate with 10 ml. of dilute (2%) HNO_3.

The procedure just outlined will yield relatively clean lead. It has been noted, however, that a dithizone

extraction of this lead is required to give a good run on the mass spectrometer.

Extraction of lead from whole rocks

Lead may be extracted from whole rocks by chemistry methods similar to that outlined for metallic sulphides. However the procedure employed here was a volatilization of lead in a furnace and is described by Cumming et al (1970). The procedure will be briefly mentioned.

Approximately 10 gm. of rock powder is mixed with 1 gm. of graphite powder and loaded in a graphite boat. The graphite boat is placed inside a quartz tube which has been sealed at one end. A short, tubular quartz stem has been glass-blown onto the quartz tube, providing a connection to a vacuum pump. A cold finger is positioned inside the quartz tube, adjacent to the sample. This assemblage is then placed inside the furnace (which consists of four silicon carbide heating elements placed inside a firebrick shell), evacuated and heated to operating temperature.

Lead which has been distilled from the sample condenses on the cold finger. This lead is dissolved in dilute HNO_3 and is purified by a dithizone extraction.

It has been observed that just a single dithizone extraction of this lead is needed to obtain a nice run on the mass spectrometer.

Lead blank

A precise determination of the total lead blank in a typical run by the use of a spike was not made. However, because of the relatively large amounts of lead present in most samples (20-50 μg) and because of the purity of the chemicals the lead blank is not thought to be significant.

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